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NEW REFRACTORY MATERIALS FOR CONSTRUCTION AND OVERHAUL OF GLASS FURANCES

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Borovichi Refractories Combine Co. has developed and mastered production of a series of new kinds of refractory articles for construction and overhaul of glass furnaces: molded packing of the bucket type for glass furnace regenerators (chamotte, mullite-corundum and periclase-spinel compositions); chamotte light-weight brick with a density of 0.9, 1.0, and 1.3 g/cm^3, with high strength; large-block articles for lining the bottom of glass furnaces; elements for the top structure, production channels, burners, and other elements of the glass furnace (based on customer plans) made of low-cement concretes. The articles have a high technical lifetime and are recommended for use in many glass works.

Borovichi Refractories Combine is well known in different sectors of industry – 149 years have passed since Emmanuel Nobel built the first Russian plant for production of "fire-resistant bricks from the fire-resistant clay found there" in Borovichi [1].

Today Borovichi Refractories Combine Co. is one of the largest modern companies in Russia in manufacture of refractories with a full production cycle and is actively introducing the most advanced scientific developments while retaining manufacture of traditional refractory products. In 2005, the combine manufactured 281,000 tons of refractories, which is 14% of all molded refractory products manufactured in Russia for the year. Borovichi Combine is second in the Russian Federation in refractory production volumes.

The Combine has traditionally manufactured aluminosilicate (chamotte, mullite, mullite–silica, mullite–corundum, corundum) articles for different applications which are well known and have been successfully used for lining the different elements of glass furnaces, brands: ShA, ShB, ShN-38, ShAM, ShV-37, ShV-42, MLS-62, MKS-72, MKV-72 [2]. Only new developments at Borovichi Refractories Combine for construction and overhaul of glass furnaces are discussed in the present article.

Mullite and mullite-corundum articles based on andalusites. Oriented toward consumer demand, in 2005 Borovichi Refractories Combine Co. implemented production of mullite and mullite-corundum articles with elevated performance characteristics (strength, porosity, deformation temperature under a load), brands MLU-62 and MKP-72. Such refractories are included in the plans of foreign firms of construction of heating units for different applications, including glass furnaces. The physicochemical properties of andalusite articles are reported in Table 1.

High-quality imported raw materials (andalusites) and modern molding equipment are used for manufacturing these items.

Light-weight heat-insulating articles. In 2005, Borovichi Combine began production of light-weight heat-insulating items with high strength which not only play the role of heat insulation for the furnace but also withstand structural loads [3]. The physicochemical indexes of refractory chamotte light-weight construction items are reported in Table 2.

TABLE 1

Index*	Item	
	MLU-62	MKP-72
Mass fraction, %:		
Al_2O_3, min	62	72
Fe_2O_3, max	1.0	1.2
Open porosity, %, max	19	16
Compressive strength, N/mm^2, min	50	70
Initial softening point, °C, min	1650	1700
Additional linear shrinkage,* %, max	0.5 (1500)	0.2 (1600)
Thermal stability, number of heating-cooling cycles (1300°C – water), min	100	100
TCLE, 10^{-6} K^{-1}	5.0	6.0
Thermal conductivity, W/(m · K)*	1.6 (720)	1.9 (740)

[1] Borovichi Refractories Combine OJSC, Novgorod oblast, Russia.

* The temperature, °C, is indicated in parentheses.

TABLE 2

Index*	Standard for articles			
	ShLK-1.3-13	ShLK-1.3-10	ShLK-1.0-8	ShLK-0.9-7
Apparent density, g/cm^3, max	1.3	1.3	1.0	0.9
Compressive strength, N/mm^2, min	13	10	8	7
Thermal conductivity, W/(m · K), max, at average temperature of 650°C	0.90	0.70	0.65	0.55
Residual changes in size of no more than 1.0% in repeated heating at temperature, °C	1300	1300	1300	1270
Deformation temperature, °C, under 0.05 N/mm^2 load	1320	1320	1270	1240

* In all items, the mass fraction of Al_2O_3 is a minimum of 30%.

TABLE 3

Index	ShL-1.3 articles	
	Requirements of GOST 5040–96	Real values
Apparent density, g/cm^3	Max 1.3	1.24
Compressive strength, MPa	Min 3.5	10.2
Additional linear shrinkage, %, at 1300°C	Max 1.0	0.1
Thermal conductivity, W/(m · K), at, °C:		
320 ± 25	Max 0.6	0.34
650 ± 25	Max 0.7	0.48

Light-weight ShLK heat-insulating refractories are manufactured in the form of rectangular, wedge, and abutment articles, slabs, and according to customer designs. Such refractories are used for heat insulating of the bottom and walls of the furnace tank. In 6 months in 2006, ShLK-0.9-7, ShLK-1.0, and ShLK-1.3 refractories were shipped to Borsk Glass Works, Klin-Steklotara Co., Belevrotara Co., Tver'-stekloplastik Co., Borisov Crystal Factory, and other sector enterprises.

In 1994, specialists in the Central Plant Laboratory at Borovichi Refractories Combine developed and patented technology for production of light-weight chamotte refractories ShL-1.3 with the plastic method of molding using foamed polystyrene as burnout additive. The use of foamed polystyrene allowed optimizing the structure of ShL-1.3 articles, significantly improving their thermomechanical and heat-insulating properties, which were much higher than the requirements in GOST 5040–96 (Table 3). Articles with such strength are also used in supporting structures and the working layer of furnace lining.

TABLE 4

Index	Article		
	ShSU-33	MLS-62	MKS-72
Mass fraction, %:			
Al_2O_3, min	33	62	72
Fe_2O_3, max	–	1.5	1.5
Additional linear shrinkage, %, max, at, °C:			
1400	0.4	–	–
1500	–	0.4	–
1600	–	–	1.0
Open porosity, %, max	18	24	24
Compressive strength, N/mm^2, min	25	25	30
Temperature of initial deformation under load, °C, min	–	1450	1500
Apparent density, g/cm^3, min	–	2.3	2.4

The company manufactures refractories with the indicated characteristic of not only standard shapes and sizes but also according to customer designs, including slabs measuring 500 × 500 × 100 mm and others, which are frequently contained in modern glass furnace designs.

In 2005 and 2006, ShL-1.3 light-weight heating-insulating articles manufactured by Borovichi Refractories Combined were sold for construction of glass furnaces at Chagodoshchensk Glass Works and Belstekloprom Co., Lunacharskii Glass Works, Salavatsteklo Co., Velikodvorsk Glass Works, Experimental Glass Works, and RASKO.

Production of large-block items for lining the bottom of the glass furnace. In 2005, Borovichi Refractories Combine purchased press equipment for manufacturing bottom block from Podol'sk Refractory Plant. Production of the large block articles ShSU-33 according to GOST 7151–74 with amendments 1 – 3, MLS-62, MKS-72 according to GOST 24704–94 for lining the bottom of glass furnaces began in the third quarter of 2006. The physicochemical indexes of the aluminosilicate refractories for construction and overhaul of glass furnaces are reported in Table 4.

To improve the geometric characteristics of the bottom block, modern imported polishing equipment for polishing refractory articles were purchased. Polishing allows manufacturing bottom block with an accuracy of up to 1 mm, so that the Combine completely satisfies customer requirements for the geometric parameters of the articles.

The Combine has mastered production of cement-free (not containing CaO) concretes for articles, including large-block articles, used in the lining of glass furnaces in order to not interrupt deliveries of bottom block. Articles made of Borovichi Refractories Combine's cement-free concretes are obligatorily fired at a minimum temperature of 1300°C during fabrication, and the internal structure of the articles is improved and possible production flaws are revealed.

TABLE 5

Index	Standard for low-cement concrete*					
	ShBT-1	ShBT-2	MLBT	MKBT	KBT	KShBT
Type of filler	Chamotte		Mullite	Mullite–corundum	Corundum	Corundum–spinel
Mass fraction in calcined substance, %:						
Al_2O_3, min	50.0	55.0	60.0	80.0	96.0	94.0
aluminmagnesia spinel, min	–	–	–	–	–	3
Fe_2O_3, max	1.7	1.5	1.0	1.5	0.5	1
CaO	1.0 – 2.0	1.0 – 2.0	–	1.0 – 2.0	1.0 – 2.0	0.5 – 2.0
Open porosity, %, max	23	22	19	22	22	22
Compressive strength in dried state, N/mm^2, min	30	35	50	35	30	30
Additional linear shrinkage, %, max, at temperature of, °C:						
1400	0.8	–	–	–	–	–
1450	–	0.8	–	–	–	–
1500			–	1.0		–
1600	–	–	–	–	0.8	–
Thermal stability, number of heating-cooling cycles (1300°C – water), min			Not regulated			25
Initial melting point, °C, min	–	–	1650	–	–	1650

* ShBT-1, ShBT-2, MKBT, KBT concretes were made according to TU 14-194-221–98 with Amendment 1, while MLTB and KShTB concretes were manufactured according to the technical agreement between customer and manufacturer.

Characteristics of mullite-silica products from Borovichi Combine for lining the bottom and walls of glass furnaces

Index	MKRS-50
Mass fraction, %:	
Al_2O_3, min	50
Fe_2O_3, max	1.5
CaO, max	0
Open porosity, %, max	22
Compressive strength, N/mm^2, min	30
Initial melting point, °C, min	1500
Additional linear shrinkage, %, at 1400°C	0.3

In 2006, a large lot of MKRS-50 large-block articles manufactured with cement-free technology was shipped to Kishinev Glass Works.

Thixotropic Concrete Articles. One trend in technical progress in equipment for industrial furnaces is validly considered the use of refractory concretes, which allows significantly simplifying and mechanizing the lining process and simplifying and reducing the manufacturing cost of refractories of complex configuration without use of molding equipment.

To ensure unlimited storage time and prevent destruction of thixotropic concrete articles on heating during use, Borovichi Refractories Combine Co. conducts preliminary firing at a temperature above 1300°C. In comparison to traditional chamotte, high-alumina, and other refractories used in the individual units of glass furnaces, the thixotropic concrete articles have much higher physicochemical indexes [4].

Together with Center–Glass–Gas SPC Co., studies were conducted at the base of the Borovichi Combine Research Center concerning the glass stability of samples of different kinds of refractories, including those made from thixotropic concretes, and the results of the studies are being actively utilized. The feeder channel sections, overlap plates, slide valves, and other production channel elements are made at the Combine and delivered to Dmitrov, Ul'yanovsk, Ekran (Novosibirsk), Svet Co. (Moscow), Kvarts Co. (Uzbekistan), and other works.

The technical characteristics of low-cement (thixotropic) concretes are reported in Table 5.

KShBT burner blocks are highly recommended. They are made with melted aluminomagnesia spinel, which allows significantly increasing the thermal stability of the concretes. KShBT burner blocks have been supplied to Chagodoshchensk, Tver', and Kamyshen plants, Svet Co. (Mozhga), Saratovstroisteklo Co., and other enterprises in the sector.

Refractories for Glass Furnace Regenerators. In 2000, Borovichi Refractories Combine Co. began production of periclase-spinel refractories – a new generation of refractories with indexes as good as the best European analogs.

Borovichi Combine uses quality raw materials for manufacturing the periclase-spinel refractories: high-purity sintered periclase with a MgO content ≥ 97% and melted (previously sintered) aluminomagnesia spinel with a total (Al_2O_3 + MgO) content ≥ 97%; adding it decreases the TCLE and increases the thermal stability of periclase articles. A distinctive feature of melted $MgAl_2O_4$ spinel is high resistance to alkali melts, alkali-containing materials, acids, carbon, and alkaline-earth oxides. To increase the resistance of refractories for lining the upper row of regenerator pack-

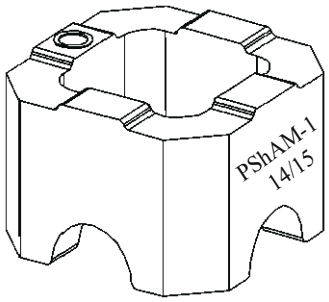

Fig. 1. One shape of molded packing for the glass furnace regenerator.

ing in glass furnaces, a periclase-spinel refractory based on melted high-purity periclase with a MgO content ≥ 96% and melted aluminomagnesia spinel with a total (Al_2O_3 + MgO) content ≥ 97% was developed at the Technology and Production Improvement Center at Borovichi Refractories Combine. The melted periclase significantly increases the corrosion resistance of the refractory, since the melted periclase crystals are much larger than sintered periclase crystals, which ensures a smaller number of boundaries where the reagent that causes corrosion can penetrate into the refractory. The new material is called PShAM-2. The physicochemical indexes of the refractories for glass-furnace regenerator packing are reported in Table 6.

In 2003, a batch of PShAM-1 refractories was delivered to Saratovstroisteklo Co. and the test results were positive [5]. In 2004 and 2005, periclase-spinel refractories were delivered for packing Kamennyi Vek Co.'s regenerators (Dubna) for use as regenerator packing in the basalt fibres palling furnace. In 2004, 2005, and 2006, molded packing refractories, including periclase-spinel refractories, were delivered to glass works for regenerator packing.

One trend in improving furnace design and increasing furnace efficiency is to use molded regenerator packing elements made of modern refractory materials (see Fig. 1). Electromelted, cross-shaped or pot(cup)-shaped periclase and periclase-zirconium refractories are most common abroad. Their use ensures high heat transfer and uninterrupted operation of the regenerator during the entire furnace campaign. Chamotte or mullite refractories are used for colder regenerator zones.

In our country, domestic rectangular chamotte and less frequently mullite and periclase refractories were basically manufactured and used until recently [6]. In recent years, modern packing refractories began to be brought in from abroad.

Borovichi Refractories Combine was one of the first to master production of molded articles for glass furnace regenerator packing and delivered them to the following glass works:

Klin-Steklotara Co. (ShV-37) – for three furnaces in 2004, 2005, and 2006;

Vasil'evo Glass Works, Tatarstan (ShV-37, MKV-72, PShAM-1) – 2005;

Svet Co., an affiliate of OSRAM Co., Smolensk (ShV-37, MKV-72) – 2005;

TABLE 6

Index	Refractory				
	GOST 20901–75 with Amend. 1 – 5			TU 14-194-251–02 with Amend. 1	
	ShV-37	ShV-42	MKV-72	PShAM-1	PShAM-2
Mass fraction, %:					
Al_2O_3, min	37.0	42.0	72.0	4.0 – 8.0	6.0 – 10.0
MgO, min	–	–	–	87.0	85.0
CaO, max	–	–	–	1.5	2.0
SiO_2, max		Not regulated		1.0	1.3
ZrO_2		Same		1.0 – 3.0	1.0 – 3.0
Fe_2O_3, max	Not standardized	1.7	1.2	1.0	1.3
Refractoriness, °C, min	1730	1750		Not regulated	
Additional linear shrinkage in holding for 2 h, %, max, at temperatures of, °C					
1350	0.2	–	–	–	–
1450	–	0.4	–	–	–
1600	–	–	0.8	–	–
1650	–	–	–	0.7	0.5
Open porosity, %, max	23	14 – 20	21	17	17
Compressive strength, N/mm^2, min	20	40	50	40	50
Initial deformation temperature under load, °C, min	1330	1500	1550	1690	1690
Apparent density, g/cm^3, min		Not regulated		2.9	3.0
Thermal stability, number of heating-cooling cycles (1300°C – water), min		Same		7	10

TABLE 7

Format*	Channel width, mm	Height, mm
14/12	140	120
14/15	140	150
17/12	170	120
17/15	170	150

* The wall thickness is 40 mm in all cases.

Grodno Glass Works Co., Belarus' (ShV-37, PShAM-1) – 2005;

Svet Co., Mozhga (ShV-37, MKV-72, PShAM-1) – 2006;

Kishinev Glass Works Co. (ShV-42, MKV-72, PShAM-1) – 2006;

Kamyshin Glass Works Co. (ShV-37, PShAM-1) – 2006.

The format of the molded refractory items is shown in Table 7.

By agreement with the customer, refractories of other sizes can be manufactured for glass furnace regenerator packing.

Molded refractories for glass furnace regenerator packing from Borovichi Refractories Combine, used alone and together with packing from Magnezit Combine, have received positive reviews from the users and are successfully replacing the expensive imported analogs [7].

Borovichi Refractories Combine Co. manufacturers a wide spectrum of traditional aluminosilicate refractory materials for construction and overhaul of glass furnaces and is actively working on new kinds of refractory products:

molded packing for glass furnace regenerators (chamotte, mullite-corundum, and periclase-spinel compositions);

chamotte light-weight brick with a density of 0.9, 1.0, and 1.3 g/cm^3 and high strength;

large-block items for lining the bottom of glass furnaces (ShSU-33, MLS-62, MKS-72, MKRS-50).

Upper structural elements, production channels, burner equipment, and other glass furnace elements made according to customer designs are being manufactured from thixotropic concretes.

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